

"A PROCESS FOR THE PRODUCTION OF NIOBIUM  
AND/OR TANTALUM POWDER WITH LARGE SURFACE AREA".

The present invention refers to a process for the production of  
5 niobium and/or tantalum powder by means of reduction of a controlled  
layer of niobium and/or tantalum oxide ( $\text{Nb}_x\text{O}_y$ , and/or  $\text{Ta}_x\text{O}_y$ , where  $x =$   
1 to 2 and  $y = 1$  to 5) deliberately formed over particles of metallic niobium  
and/or tantalum and/or hydrides thereof of high purity by a reaction metal  
dissolved in a solution of molten salts in a controlled atmosphere.

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The reduction of oxides of niobium and/or other refractory  
metals by metals and/or hydrides of alkali metals or alkali earth metals is  
well known, as may be noted in Patents Nos. US 1,728,941, US  
2,516,863, US 4,687,632, US 6,136,062, US 6,171,363, DE 19831280 and  
15 WO 00/15555.

The main problem of the metalloceral reaction is its  
strongly exothermal and uncontrolled reaction, causing an excessive  
heating of the system and impairing the characteristics of the powder that is  
20 produced (increase in mean particle size and decrease of specific area).

One of the manners of controlling the reaction is to perform  
the reduction initially to a sub-oxide of niobium, such as described in some  
patents, since in this condition the exothermal characteristic of the reaction  
25 is less intense. The sub-oxide thus produced would then be reduced to  
metallic niobium, again with less intense exothermal behavior, producing a  
powder with the recommended characteristics. However, such procedure

creates a need to conduct the process in two stages, requiring an increased consumption of energy and time. Furthermore, the possibility of contamination of the powder is increased due to the greater number of stages under high temperatures in contact with the oven atmosphere, with  
5 the reducing agent and with the container where the reaction takes place. Some patents mention the need to use forced cooling of the reactor and/or use of mechanical stirring devices, in order to decrease the exothermal effect of the reaction and to promote the dissipation of heat. One other form of reaction that is mentioned consists in the use of the alkali metal or earth  
10 metal in the form of vapor. The use of a vapor is justified to solve the problems that occur when the reducer is used in the liquid state. However, the use of this technique frequently entails a need to conduct subsequent deoxidizing steps, since one most always fails to achieve a full reduction in one sole step. Furthermore, although the vaporization of alkali metals or  
15 earth alkali metals is endothermic, the reduction of the niobium oxides through the use of these metals in the form of vapor is more exothermal than when they are used in liquid form. This is detrimental to the control of the reaction towards avoiding overheating.

20           The use of the technique of reduction in molten salts is cited for the production of niobium and/or other refractory metals, however employing other sources of niobium such as potassium fluoroniobate, using sodium as a reducing agent (US Patent No. 4,684,399), or reducing this same compound with sodium using as diluent a bath of molten salts  
25 comprised of KCl-KF or KCl-NaCl (WO 01/59166) and niobium pentachloride reduced by reaction metals dissolved in a solution of molten salts (US Patent No. 4,725,312 and WO 01/59166).

The process disclosed in US Patent No. 4,725,312 and WO 01/59166 proposes a process for the production of metals in powder form of groups IV-B and V-B of the Periodic Table of Elements (US Patent No. 4,725,312) by reducing the salts of those metals through the use of a bath 5 of molten salts containing lithium as the reducing agent. A wide range of binary mixtures of salts is mentioned, among which there should be pointed out: LiCl-KCl, CsCl-LiCl, RbCl-LiBr and KBr-LiBr, LiCl-NaCl-CsCl, LiCl-NaCl-RbCl and LiCl-KCl-KF. In this process the bath of salts is kept at a temperature between 400 and 550°C. The quantity of lithium present in 10 the bath of molten salts should at least be the stoichiometric amount required for the reduction of the chlorides of Nb, Ti and Nd, and these chlorides may be introduced in solid, liquid or gas form, this latter being preferred.

15 The patent application publications Nos. WO 01/82318 and WO 01/59166 mention the production of niobium powders by means of the reduction of K<sub>2</sub>NbF<sub>7</sub> using sodium as the reducing agent added to a bath of molten salts (KCl-KF or KCl-NaCl).

20 The main advantages of the use of the method of reduction in molten salts are: a) the dissipation of the heat generated in the reaction occurs in the bath of salts thus avoiding localized overheating; b) it is possible to control the reducing potential of the reducing agent by means of the dissolution thereof in a molten salt; c) it is possible to continuously feed 25 both the reducing agent and the raw material containing Nb and/or Ta to the salts bath and thereby to control the speed of reduction and therefore the generation of heat; d) avoiding direct contact between the reducing

agent and the source of Nb and/or Ta, decreasing the possibility of sintering and inadequate growth of the powder of Nb and/or Ta thus reduced; e) it is possible to stir the bath of salts, and therefore to allow control over the speed of the reaction increasing or decreasing the rate of dissolution both of  
5 the reducing agent and of the source of Nb and/or Ta in the molten salt; f) it is possible to control the reaction temperature by proper selection of a salt solution which melting temperature is compatible with the temperature at which it is desired to conduct the reaction; g) easy recovery of the powder of Nb and/or Ta thus produced, since it is merely necessary to dissolve the  
10 salt in an aqueous solution to recover the same; h) the oxides of alkali metals or earth alkali metals dissolve in the salt preventing the formation of barriers between the reagent and the reducing agent; i) it is not necessary to use the reducing agent in powdered or granulated form; j) it is possible to introduce a doping element – nitrogen in the Nb and/or the Ta, through the  
15 atmosphere of the oven that keeps the salt in the molten state, either by injecting N<sub>2</sub> gas into the bath of salts or by means of agents that carry the doping element and which may dissolve in the molten salt and k) it is possible to introduce a doping element – phosphorus in the Nb and/or the Ta, by means of agents that carry the doping element which may dissolve  
20 in the molten salt.

With this method, the oxide of niobium and/or tantalum may be reduced in a controlled manner with a strong reducing agent producing a power of high purity, with a sponge-like morphology, of low apparent density and large specific surface area. Additionally, since the raw material  
25 is a metallic niobium and/or tantalum powder and/or hydrides thereof of high purity and adequate size, that was previously oxidized in a controlled

manner to have an adequate layer of oxide, the thermal energy generated in the reduction of this layer of oxide is much less than that which would be generated to obtain the same particle if the raw material was to consist entirely in oxide. This lesser generation of energy facilitates the control of  
5 the process such that the possibility of contamination by gasses and other metals is significantly reduced, which may be evidenced by the low leakage current of the powder obtained using this process.

#### **DETAILED DESCRIPTION OF THE INVENTION**

10 The present invention comprises a process for the production of metallic powder of niobium and/or tantalum by means of metallothermal reduction in molten salts wherein the problems of overheating during the reduction, or of the need to conduct the process in more than one step, are eliminated.

15 With such procedure, it is possible to control and to dissipate the heat generated in the mixture due to the presence of the salts bath, to control the speed of the reaction, by controlling the feed rate of the reagents and avoiding direct contact of the reducing agent with the reagent. In  
20 addition to the thermal aspect, the reaction is more controlled due to the possibility of controlling the potential of the reducing agent, due to the same being diluted in the salt at the desired concentration. In this manner, the driving force for the reduction may be controlled, allowing increased control of the process. The use of a raw material in the form of a powder,  
25 of adequate size, consisting basically in metallic niobium and/or tantalum and/or hydrides thereof, of high purity, previously oxidized in a controlled manner (hereinafter referred as "oxidized powder"), leads to a uniform

precipitation of the Nb and/or the Ta, with the aspect of a sponge, within the medium of liquid salt, producing an adequate distribution of particles without the formation of clusters of undesirable size.

5           The reducing agent is an alkali or earth alkali metal, preferably calcium or magnesium and/or a hydride of such metal. Nitrides of alkali metals or earth alkali metals may also be fed to the reactor constituting sources of N<sub>2</sub> for the produced niobium and/or tantalum.

10          The reduction occurs at temperatures between 300 and 1200° C, preferably between 500 and 1000° C in an inert atmosphere (argon or helium) or a reactive atmosphere containing, for example, nitrogen (N<sub>2</sub>).

15          During the reduction, the salt may be subjected to mechanical stirring or to the injection of an inert or partially inert gas containing, for example, N<sub>2</sub>. The molten salt may be comprised of mixtures of salts or of pure salts, such as fluorides and chlorides of Ca, Li, Ba, Mg, K and Na. The salts evidencing greater solubility of the reducing agent are preferred, such as CaCl<sub>2</sub> when employing calcium as reducing agent.

20          The reducing agent and the oxidized Nb and/or Ta powder may be continuously fed to the molten salt using devices that allow to control the feed rate of both. The temperature of the process may be kept constant by controlling the feed rate of the raw materials. The quantity of  
25         reducing agent that is used should be at least the stoichiometric amount for the reduction of all the oxide of the oxidized powder of Nb and/or Ta that is fed. There may be employed a quantity up to 800% of the stoichiometric

amount. Such excess depends, among other parameters, on the quantity of salts bath.

Both the reducing agent and the "oxidized powder" may be  
5 added together with the salt bath to the reduction reactor prior to the melting step or may be fed separately or together to the salt bath upon the prior melting thereof. This feeding may be carried out continuously or otherwise. The quantity of reducing agent is substantially less in comparison to the reduction of particles of oxides, and depending on the  
10 oxygen content of the oxidized powder, the required quantity of reducing agent may be previously added to the salt bath.

Normally the following salts or mixtures thereof are employed to control the reaction: CaCl<sub>2</sub>, NaCl, KCl and MgCl<sub>2</sub>. The mixture of salts  
15 allows the reduction to occur at a lower temperature, allowing to obtain smaller particle sizes and larger surface areas. The quantity of salt or mixture of salts will have an effect on the control of the reaction temperature, the greater is the quantity of salt the easier it will be to control the temperature. The quantity of salt used may vary between 5 and 100g/g  
20 of oxidized powder fed.

The reaction may be carried out in stainless steel, nickel, tantalum or niobium reactors, depending on the degree of contamination that can be tolerated in the product obtained.

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After the reaction, the resulting salt mixture containing metallic niobium and/or tantalum is dissolved in deionized water and is

subsequently filtered and leached with a solution containing HCl and which may also contain HF, HNO<sub>3</sub> and H<sub>2</sub>SO<sub>4</sub>. After the leaching the material is rinsed and dried.

5                 The amount of water for solubilization of the salt varies between 10 and 100 liters for every 5 kg of salt. For the acid leaching step there are used 1 to 100 ml of solution for every gram of powder obtained from dissolution of the salt.

10                 The control of the nitrogen content in the Nb and/or Ta may be effected by controlling the partial pressure of N<sub>2</sub> in the atmosphere of the oven, by an injection of N<sub>2</sub> gas or of mixtures of gasses containing N<sub>2</sub> into the molten salt, or yet, by the addition of N<sub>2</sub> carrier elements, such as nitrides soluble in the molten salt. A part of the nitrogen is dissolved in the  
15                 solution of salts allowing that nitride ions may be available to allow the solubilization of nitrogen in the particles of Nb and/or Ta. Similarly, it is possible to dope with phosphorus by adding phosphorus compounds soluble in the salt bath.

20                 The particles of powder of Nb and/or Ta produced using the present process have a reduced size, have a large surface area and a sponge-like morphology, and are adequate for the production of capacitors.

25                 The reducing procedure consists in melting the salt initially in a stainless steel, nickel, niobium or tantalum reactor, either or not in the presence of the oxidized powder, and of the reducing agent in an inert gas atmosphere. Before the heating of the reactor, the oven chamber should be

evacuated and then pressurized with the inert gas at pressures that may vary from 400 to 1200 torr. After the salt is molten, the temperature is stabilized between 30 and 150° C above the melting point of the salt or of the reducing metal, whichever has the higher melting point. From this moment 5 on there is started the stirring process of the bath using a mechanical agitator or by means of injection of an inert or reactive gas (N<sub>2</sub> or a mixture of N<sub>2</sub> with an inert gas). If the reducing agent and/or the "oxidized powder" have not been previously added, there is initiated the addition of both or of one of them using an adequate system that allows to control the 10 feed rate to the salt bath.

After having awaited the time required for reaction, the stirring is discontinued and the oven is turned off to allow the cooling of the salt containing metallic Nb and/or Ta.

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The time required for the reduction will depend on the feed rate of the reducing agent or the oxidized powder, or yet of the quantity of powder and reducer fed together with the salt prior to the beginning of the reaction.

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The feed rate of the oxidized powder is an important parameter for the control of the process, since it may control the localized generation of heat. However, as previously explained, this amount of heat is substantially less when compared to the use of oxide of Nb and/or Ta as 25 source of Nb and/or Ta.

The reduction temperature may have an influence on the

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surface area of the produced powder. Higher temperatures may lead to larger particles with lesser specific surfaces. Therefore, the selection of the mixture of salts is important with a view to lowering the temperature of the process.

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Stirring the salt is also important to avoid localized overheating and to disperse the oxidized powder, avoiding its segregation in the bath.

## 10 BRIEF DESCRIPTION OF THE DRAWINGS

The present invention is described with further detail in reference to the attached Figures, wherein identical numerals represent identical structures throughout the various drawings, and wherein:

15 Figure 1 is a schematic drawing of a reactor for reduction of the oxidized powder;

Figure 2 depicts a detail of the support stem inside the crucible; and

20 Figure 3 illustrates back-scattered electrons of the typical morphology of powders produced using the processes set forth herein.

Figure 1 is a schematic drawing of the reactor used for the reduction in molten salts where the oxidized powder is continuously fed in a crucible containing a molten salt. In the same crucible that contains the salt, there is placed another container, submerged in the salt, containing the liquid alkali metal or earth alkali metal. The identifications of Figure 1 are:  
25 1- Crucible containing the liquid alkali metal or earth alkali metal; 2-

Crucible containing the molten salt; 3- Stirring stem; 4- Molten salt; 5- Inert or reactive gas inlet; 6- "oxidized powder"; 7- Container with the "oxidized powder" contained therein; 8- Thermocouple; 9- Oven chamber and 10- Vacuum system outlet.

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In this system, the mechanical stirring may be substituted by stirring caused by injection of an inert or reactive gas.

After cooling of the reactor in an inert atmosphere, the  
10 produced material is dissolved in deionized water. The solution obtained in the dissolution of the salt is filtered, and is then leached in a solution containing HCl, HNO<sub>3</sub>, H<sub>2</sub>SO<sub>4</sub> and HF. The amount of leaching solution employed is 1 to 100 ml/g of filtered product, preferably 10 to 40 ml/g. After this leaching, there is performed a final rinsing with deionized water,  
15 filtration and subsequently, vacuum-drying.

According to the present invention, the powder of Nb and/or Ta obtained has contents of Mg and Ca below 500 ppm, sodium content below 50 ppm, oxygen content between 1,000 and 4,000 ppm/(m<sup>2</sup>/g), sum  
20 total of contents of Fe, Cr and Ni below 300 ppm and a specific surface area between 1 and 30 m<sup>2</sup>/g.

The present invention is illustrated in further detail by means of the examples described in the following:

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**Example 1:**

A closed reactor as depicted in Figure 1, containing inside the

same another container with 124 g of metallic calcium among 4 kg of calcium chloride, was subjected to heating in an argon atmosphere (800 torr.) to a temperature of 900° C. After homogenization of this mixture by means of mechanical stirring, 100 g of "oxidized powder" (average particle size 2.3 microns) was added in continuous fashion. After the reduction, the mixture was cooled down to ambient temperature.

The material was removed from the reactor and subjected to dissolution in deionized water. The solid phase was leached with an aqueous solution containing HCl and HF for 90 minutes. This mixture was then filtered and rinsed with 10 liters of deionized water. The cake obtained from filtration was subsequently vacuum-dried. The chemical analysis of the obtained powder evidenced that the oxygen content had fallen from 18,000 ppm to 3,850 ppm.

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**Example 2:**

A closed reactor as depicted in Figure 1, containing inside the same another container with 124 g of metallic calcium among 4 kg of calcium chloride, was subjected to heating in an argon atmosphere (800 torr.) to a temperature of 900° C. After homogenization of this mixture by means of mechanical stirring, 100 g of "oxidized powder" (average particle size 18.6 microns) was added in continuous fashion. After the reduction, the mixture was cooled down to ambient temperature.

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The material was removed from the reactor and subjected to dissolution in deionized water. The solid phase was leached with an aqueous solution containing HCl and HF for 90 minutes. This mixture was

then filtered and rinsed with 10 liters of deionized water. The cake obtained from filtration was subsequently vacuum-dried. The chemical analysis of the obtained powder evidenced that the oxygen content had fallen from 6,300 ppm to 785 ppm.

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**Example 3:**

A closed reactor as depicted in Figure 1, containing inside the same another container with 124 g of metallic calcium among 4 kg of calcium chloride, was subjected to heating in an argon atmosphere (800 torr.) to a temperature of 900° C. After homogenization of this mixture by means of mechanical stirring, 100 g of "oxidized powder" (average particle size 1.1 micron) was added in continuous fashion. After the reduction, the mixture was cooled down to ambient temperature.

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The material was removed from the reactor and subjected to dissolution in deionized water. The solid phase was leached with an aqueous solution containing HCl and HF for 90 minutes. This mixture was then filtered and rinsed with 10 liters of deionized water. The cake obtained from filtration was subsequently vacuum-dried. The chemical analysis of the obtained powder evidenced that the oxygen content had fallen from 52,210 ppm to 10,500 ppm (equivalent to 4,565 ppm/(m<sup>2</sup>/g)).

**Example 4:**

A closed reactor as depicted in Figure 1, containing inside the same another container with 40 g of metallic magnesium in a mixture of 3.2 kg of calcium chloride and 0.8 kg of potassium chloride, was subjected to heating in an argon atmosphere (800 torr.) to a temperature of 900° C.

After homogenization of this mixture by means of mechanical stirring, 100 g of "oxidized powder" (average particle size 1.9 micron) was added in continuous fashion. After the reduction, the mixture was cooled down to ambient temperature.

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The material was removed from the reactor and subjected to dissolution in deionized water. The solid phase was leached with an aqueous solution containing HCl and HF for 90 minutes. This mixture was then filtered and rinsed with 10 liters of deionized water. The cake obtained 10 from filtration was subsequently vacuum-dried. The chemical analysis of the obtained powder evidenced that the oxygen content had fallen from 39,620 ppm to 6,700 ppm (equivalent to 4,188 ppm/(m<sup>2</sup>/g)).

**Example 5:**

15 The oxidized powder (11 g) was placed on a metallic screen, attached to the support stem (11), inside a crucible 1, as shown in Figure 2. The metallic magnesium (25 g) was placed in the reducer container (Ca/Mg, NbH), also attached to the support stem (2). The mixture of calcium chloride (240 g) and potassium chloride (60 g) was placed inside 20 the crucible, together with the oxidized powder and the metallic magnesium. The crucible was sealed, there being welded a cover thereon. The mixture was heated to a temperature of 900° C for 2 hours. After the reduction, the mixture was cooled down to ambient temperature.

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The material was removed from the crucible and dissolved in deionized water. The solid phase was leached with an aqueous solution containing HCl and HF for 90 minutes. This mixture was then filtered and

rinsed with deionized water. The cake obtained from filtration was subsequently vacuum-dried. The chemical analysis of the obtained powder evidenced that the oxygen content had fallen from 52,210 ppm to 5,850 ppm (equivalent to 3,250 ppm/(m<sup>2</sup>/g)).

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**Example 6:**

The oxidized powder (11 g) was placed on a metallic screen, attached to the support stem (11), inside a crucible (1), as shown in Figure 2. The metallic calcium (25 g) was placed in the reducer container (Ca/Mg, 10 NbH), also attached to the support stem. The calcium chloride (300 g) was placed inside the crucible, together with the oxidized powder and the metallic calcium. The crucible was sealed, there being welded a cover thereon. The mixture was heated to a temperature of 900° C for 2 hours. After the reduction, the mixture was cooled down to ambient temperature.

15

The material was removed from the crucible and dissolved in deionized water. The solid phase was leached with an aqueous solution containing HCl and HF for 90 minutes. This mixture was then filtered and rinsed with deionized water. The cake obtained from filtration was 20 subsequently vacuum-dried. The chemical analysis of the obtained powder evidenced that the oxygen content had fallen from 52,210 ppm to 5,520 ppm (equivalent to 3,070 ppm/(m<sup>2</sup>/g)).

The typical morphology of the powders produced using the 25 processes set forth herein may be seen in the image of back-scattered electrons shown in Figure 3.